

High Temperature Thermosetting Polyimide Nanocomposites Prepared with Reduced Charge Organoclay

Sandi Campbell¹ and Margaret I. Liang²

¹ NASA Glenn Research Center, Cleveland, OH. 44135

²The Ohio State University, Columbus, OH 43210

Abstract

The naturally occurring sodium and calcium cations found in bentonite clay galleries were exchanged with lithium cations. Following the cation exchange, a series of reduced charge clays were prepared by heat treatment of the lithium bentonite at 130°C, 150°C, or 170°C. Inductively coupled plasma (ICP) analysis showed that heating the lithium clay at elevated temperatures reduced its cation exchange capacity. Ion exchange of heat-treated clays with either a protonated alkyl amine or a protonated aromatic diamine resulted in decreasing amounts of the organic modifier incorporated into the lithium clay. The level of silicate dispersion in a thermosetting polyimide matrix was dependent upon the temperature of Li-clay heat treatment as well as the organic modification. In general, clays treated at 150°C or 170°C, and exchanged with protonated octadecylamine or protonated 2,2'-dimethylbenzidine (DMBZ) showed a higher degree of dispersion than clays treated at 130°C, or exchanged with protonated dodecylamine. Dynamic mechanical analysis showed little change in the storage modulus or T_g of the nanocomposites compared to the base resin. However, long term isothermal aging of the samples showed a significant decrease in the resin oxidative weight loss. Nanocomposite samples aged in air for 1000 hours at 288°C showed up to a 20% decrease in weight loss

compared to that of the base resin. This again was dependent on the temperature at which the Li-clay was heated and the choice of organic modification.

Introduction

Increasing the reliability and lifetime of aerospace polymers used for high temperature applications has been a constant challenge. There has been a significant amount of research aimed at increasing the thermo-oxidative stability (TOS) of various thermosetting polyimides by altering the structure of the dianhydride,¹ the diamine,²⁻⁴ or the end-cap⁵. An alternative to modification of the polymer, as a means of increasing TOS, is the dispersion of a layered silicate in the polymer matrix. Layered silicates have quickly become recognized as useful filler in polymer matrix composites. Their platelet morphology and high aspect ratio result in greatly improved thermal,^{6,7} mechanical,⁸⁻¹⁰ and gas diffusion barrier properties.^{11,12}

While numerous polymer-layered silicate systems have been investigated, high temperature polyimides pose a specific problem for nanocomposite preparation in that the temperatures required for polymer processing are often higher than the degradation temperature of the organic modifier.^{13,14} Consequently, low molecular weight degradation products become trapped in the thermoset matrix, which can lower modulus and reduce thermal stability. Various groups have investigated alternatives to the traditional alkyl ammonium ion modification. These have included multi-functional compounds,¹⁵ and modifiers with an increased thermal stability, such as aromatic amines¹⁶ or phosphonium ions¹⁷. Reducing the degradation of the organic modifier on the clay is necessary to achieve good thermal stability of the nanocomposite. The goal of

this work was to reduce the organic degradation products by reducing the amount of organic modifier within the layered silicate. The approach taken was to reduce the cation exchange capacity of bentonite clay. Initially, the sodium and calcium cations in clay galleries were replaced by exchange with lithium chloride. When the lithium exchanged clay was heated, the small size of the lithium cation allowed its migration from the clay interlayers to sites within the silicate sheets. This migration occurred to various extents depending upon the temperature at which the lithium clay was heated. These cations became fixed in the sheets and were thus non-exchangeable.¹⁸ Therefore, this process lowered the cation exchange capacity of the clay, allowing a smaller amount of organic material to be exchanged into the galleries. By reducing the amount of organic material that may degrade, the thermal stability of the nanocomposite should improve. DMBZ-15 was chosen as the matrix resin for this study due to its outstanding properties, particularly its high glass transition temperature and thermal stability.¹⁹

Experimental

Materials: Dodecylamine, octadecylamine, lithium chloride, and ammonium acetate were purchased from Aldrich. Bentonite (Bentolite-H, cation exchange capacity (CEC) = 90 meq/100g) was received from Southern Clay Products. 2,2'-dimethylbenzidine (DMBZ) and 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride (BTDA) were purchased from Chriskev. Nadic anhydride (NA) was acquired from TCI America. All materials were used as received.

Cation exchange (with lithium chloride): Bentonite clay (10g) and lithium chloride (10g) were mixed in 450 ml distilled water and stirred at 60°C for three hours. The lithium

exchanged clay was then filtered, washed thoroughly with distilled water, and dried overnight in a vacuum oven at 100°C. Using this clay, the exchange was repeated with an additional 10g of lithium chloride to maximize the replacement of sodium and calcium ions with lithium cations. After filtering and drying this solution, the silicate was washed thoroughly with distilled water and again dried overnight in a vacuum oven at 100°C.

Heat treatment: The lithium exchanged clay samples were heated in an air circulating oven at 130°C, 150°C, or 170°C for 24 hours. Throughout this paper, the reduced charge clays will be designated by their heat treatment temperature (130 °C, 150 °C, or 170 °C). For example, Li-0 refers to lithium-exchanged clay with no heat treatment and Li-130 denotes lithium-exchanged clay heated at 130°C for 24 hours.

Extraction/ICP: The heat-treated lithium clays (0.2g) were each sonicated in deionized water (20mL) until a homogenous clay-water suspension was obtained. Aqueous ammonium acetate (10mL, 0.10N) was added dropwise. The resulting mixture was sonicated for 10 minutes and compacted into a pellet by centrifugation. The clear supernatant was analyzed for lithium content by ICP. The remaining pellet of clay was resuspended in 20mL of water and the cycle was repeated twice. The cation exchange capacity (CEC) is identified as total number of millimoles of lithium extracted in the three washings divided by the mass of the clay.²⁰

The samples were analyzed for lithium by Inductively Coupled Plasma (ICP) Emission Spectroscopy using the Varian Vista Pro ICP Emission Spectrometer. The emission lines that were utilized were 610.365 nm for samples with lithium in the approximate range of 0.4 - 3.0 mg/L and 670.783 nm for samples with lithium in the approximate range of 0.01 - 0.5 mg/L. The two emission lines were calibrated with

dilutions of an aqueous lithium standard from Alfa Aesar which is traceable to a NIST standard.

Ion exchange of reduced charge clays: Ion exchange of the interlayer cations of the lithium clay with the hydrochloride salts of dodecylamine (B12), octadecylamine (B18), or DMBZ (B-DMBZ) was performed by dissolving the amine (5mmol) in 450 mL of a 0.005M aqueous HCl solution at 60°C. The silicate (5g) was dispersed in the solution and the resultant mixture was stirred at 60°C for three hours. The solution was filtered and the clay was washed thoroughly with distilled water at 60°C. To maximize the amount of diamine exchanged, the procedure was repeated for a total of three exchange procedures.²¹ The silicate was then dried overnight in a vacuum oven at 100°C.

DMBZ-15 and nanocomposite synthesis: The thermosetting polyimide (DMBZ-15) used for the nanocomposite matrix was prepared by reaction of 3,3',4,4'-benzophenone tetracarboxylic acid, dimethyl ester (BTDE) and 2,2'-dimethylbenzidine (DMBZ) with a nadic ester (NE) as the endcap. DMBZ-15 synthesis is illustrated in Figure 1.

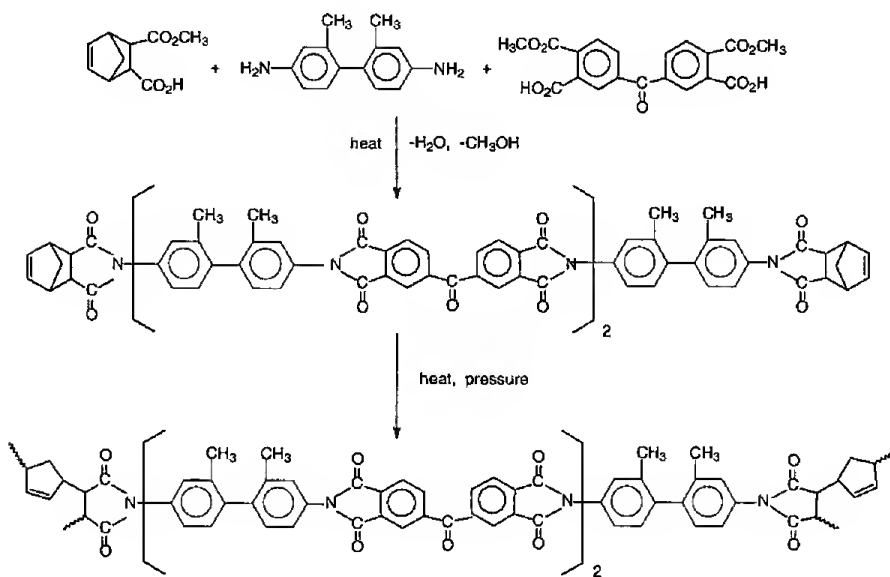


Fig 1

DMBZ-15 nanocomposites (5.0g) were prepared by room temperature mixing of BTDE (5.15g of a 50 wt% methanol solution), DMBZ (2.127g), 3 wt% clay sample (0.15g), and NE (2.61g of a 50 wt% solution in methanol). The resultant mixture was dissolved in methanol then heated at 60°C to evaporate of solvent. The remaining solution was B-staged at 400°F for two hours.

The oligomer was then cured in a mold at 315°C under 2355 psi to produce the crosslinked polymer. The polymer was post cured in an air circulating oven for 16 hours at 315°C to further crosslinking.

Wide Angle X-ray diffraction: X-ray diffraction (XRD) patterns were obtained using a Philips XRG 3100 X-ray diffractometer with Ni-filtered CuK α radiation. Heat treated clays, ion exchanged clays and B-staged DMBZ-15 nanocomposites were ground into powder and the XRD data was recorded in the range of $2\theta = 2^\circ$ to 32° .

Transmission Electron Microscopy: TEM specimens were prepared by microtoming sections of post cured DMBZ-15 nanocomposites, 100 nm thick, and floating the sections onto Cu grids. Micrographs were obtained with a Philips CM 200, using an acceleration voltage of 200 kV.

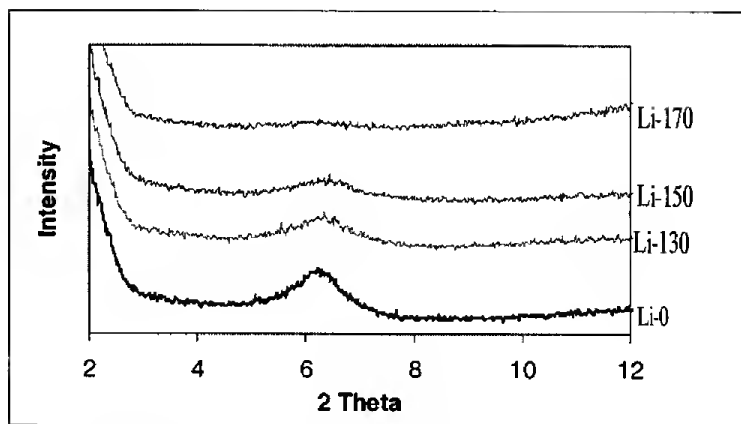
TA Instruments Thermal Gravimetric Analyzer (TGA) was used to determine the approximate amount of organic modifier present in the samples after ion exchange. The analysis was performed in air at a ramp rate of 10.0°C/min.

Thermo-Oxidative Stability: Isothermal aging of the DMBZ-15 nanocomposites was performed to determine the TOS. Post-cured samples were cut into 1.02 cm by 0.64 cm coupons and placed in an air circulating oven at 288°C for 1000 hours. The weight loss

was measured at regular intervals by removing the coupons from the oven, allowing them to cool to room temperature, and weighing the sample.

Results and Discussion

The change in silicate d_{001} spacing following heat treatment of the lithium clay was analyzed by XRD. The diffraction patterns are shown in Figure 2.



label & caption figure!

Fig 2

On heating the lithium clay, the data showed a slight shift in the position of the d_{001} peak, to a higher diffraction angle. This corresponds to a smaller d-spacing than the unheated lithium clay. The d_{001} spacing of the Li-0 sample was calculated as $d_{001} = 1.38$ nm, $2\theta = 6.41$. Li-130 exhibits a larger diffraction angle, $2\theta = 6.53$, $d_{001} = 1.35$ nm. The peak for Li-150 appears at $2\theta = 6.53$, $d_{001} = 1.34$ nm. Increasing the temperature from 130°C to 150°C did not result in as large of a peak shift as did the initial heating of samples Li-0 to Li-130. The diffraction peak of the Li-170 sample was too broad to accurately determine maximum peak position.

The data also showed a decrease in the peak intensity with increasing temperature, suggesting a breakdown of the silicate layer registry, a smaller amount of swellable inter-layers, and a lower CEC of the sample.²²

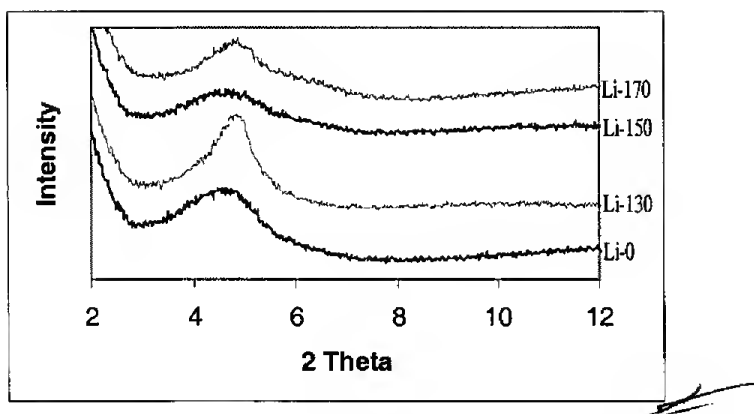
The amount of free lithium ions in each sample was determined by extraction with ammonium acetate followed by ICP analysis. The CEC of the Li-clays was then calculated and listed in Table 1.

Table 1

Sample	CEC (mmol/g)
Bentolite H (as received)	90
Li-0 (Lithium exchanged)	77
Li-130	73
Li-150	72
Li-170	71

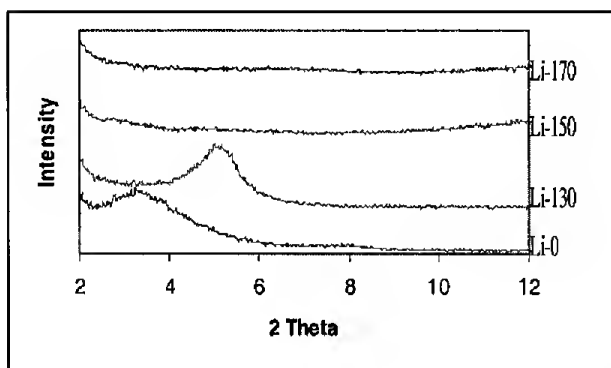
Exchanging sodium ion in the as-received silicate sample from primarily sodium to lithium lowered the CEC from 90 mmol/g to 77 mmol/g. The ion exchange procedure was carried out at 60°C, however the Li-0 sample did not receive further heat treatment. The decrease in CEC was expected with an increase in the temperature of heat treatment, as a greater number of free lithium ions migrate into the silicate layers where they remain bound and unexchangeable. Comparing the CEC of Li-0 with that of Li-130 showed a 4 mmol/g reduction, however further reductions in the heated samples were small, possibly because the temperature difference between samples was only 20°C.

Ion exchange of the reduced charge clays with an organic modifier produced varying results by XRD. Figure 3 shows the XRD patterns of clays ion exchanged with protonated dodecylamine, (B12). While there was little change in the d-spacing of the different clays, the peak intensity was low for Li-150 and Li-170, indicating a less regular stacking of the clay layers.

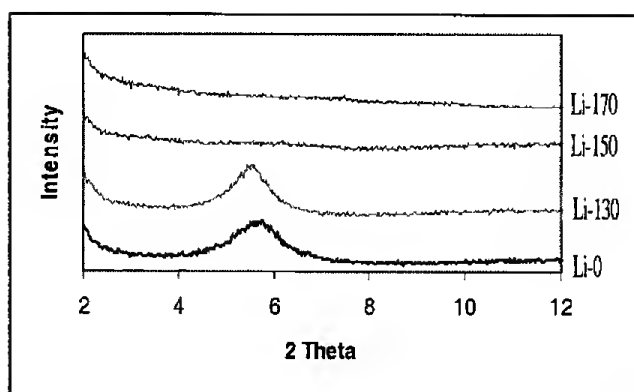


There was a slight shift in the d_{001} peak of the Li-130 and Li-170 exchanged clays, compared to the d_{001} peak from Li-0. A shift in the diffraction peak is dependent on the amount of organic modifier that has been exchanged into the clay as well as the conformation of the modifier within the gallery. A shift in the diffraction peak to a higher angle may be expected in these samples because as the CEC is reduced, the amount of ion exchange material between the layers should decrease. The reduction in the amount of organic material may allow the modifier to adopt a conformation lying parallel to the silicate surface, thereby reducing the silicate d-spacing. However, in this case, there was no clear trend with respect to the d-spacing of the clay.

The XRD patterns of Li-clay modified with protonated octadecylamine (B18) are shown in Figure 4. The diffraction data showed a reduction in the intensity of the d_{001} peak as the temperature of clay heat treatment increases. There was a clearly visible shift to a smaller angle for Li-0, compared to Li-130, due to the greater amount of modifier exchanged in the galleries. In the case of Li-150 and Li-170, there was no visible peak following ion exchange.



A common problem with using long chain aliphatic amines as an organic modifier is their low thermal stability. When dispersed in a high temperature polymer matrix, the resin processing temperatures are often greater than the degradation temperature of the aliphatic surfactant. For this reason, Li-clay was also exchanged with protonated DMBZ monomer (B-DMBZ). This diamine was tethered to the silicate at one end, while the other amine was free to react into the polymer matrix. The XRD patterns of B-DMBZ are shown in Figure 5. Again, there were no visible peaks for Li-150 and Li-170. In this case, there was a small shift in the Li-130 peak to a smaller diffraction angle relative to Li-0. This suggests an increase in the d-spacing following exchange with DMBZ.



The amount of exchangeable lithium ion present in the clay before ion exchange was calculated based on ICP analysis. Following ion exchange, the amount of modifier

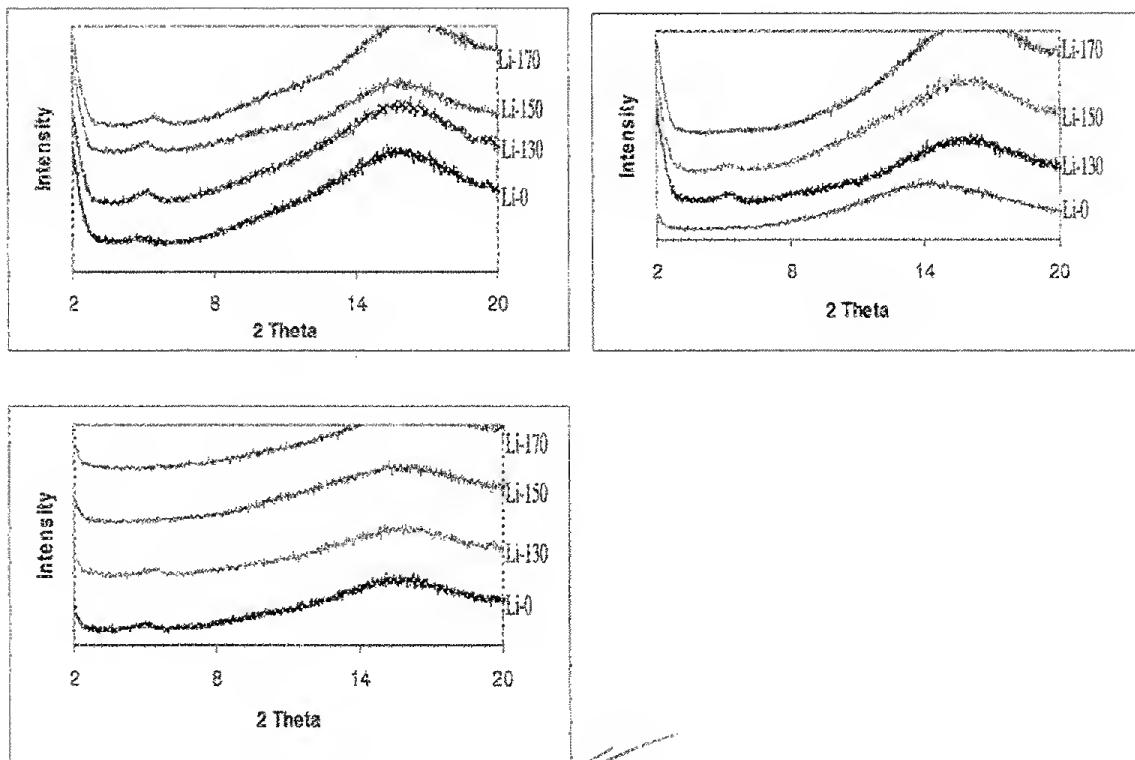
present in the clay was approximated by calculating weight loss based on TGA experiments. The TGA results are listed in Table 2.

B12	%wt loss (500°C)	B18	%wt loss (500°C)	B-DMBZ	%wt loss (500°C)
No heat	16.46	No heat	18.59	No heat	8.25
130°C	14.38	130°C	18.03	130°C	5.87
150°C	16.46	150°C	18.96	150°C	6.72
170°C	12.95	170°C	13.65	170°C	4.34

A higher weight loss by TGA signifies the presence of a greater amount of organic modifier, and therefore a higher CEC of the clay. The TGA weight loss data reveals that in nearly all instances, the CEC and TGA results were directly related, with the exception of samples heated at 150°C. In this case, the percent weight loss was higher than that of the Li-130 samples, and in some cases greater than Li-0. It is unclear at this point why the clay heated at 150°C contains a higher percentage of organic modifier than expected.

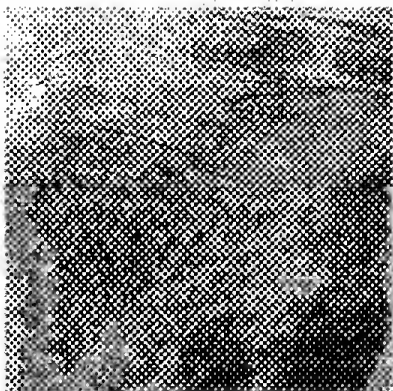
The temperature of Li-clay heat treatment, and therefore the amount of modifier in the silicate galleries, affected silicate dispersion in the DMBZ-15 matrix. The XRD data of Li-clay/ DMBZ-15 nanocomposites (Li- 0, Li-130, Li-150, and Li-170) modified with B12, B18, B-DMBZ are shown in Figures 6a-6c, respectively. The low in the intensity of the diffraction peak appearing at approximately $2\theta = 6.5^\circ$ suggests a much greater level dispersion for the Li-170 samples within each group of modifiers. The low peak intensity for clays modified with B18 or B-DMBZ, compared to B12, indicated a greater level of

dispersion of the former Li-clays in the DMBZ-15 matrix.



The dispersion of silicate in the DMBZ-15 matrix was also characterized by TEM. Representative samples including Li-0 exchanged with B12, Li-150 exchanged with B18 and Li-170 exchanged with B-DMBZ are shown in Figures 7a-7c, respectively.





The TEM image of B12 in DMBZ-15 shows silicate layers that are only partially dispersed in the resin matrix. The TEM images of the B18 and B-DMBZ show the exfoliation of layers in the matrix and confirm the trends in dispersion that were suggested by the XRD data. A greater level of silicate layer separation was achieved when the clay was heated to 150°C or 170°C, and exchanged with B18 or B-DMBZ.

Both the thermal stability of the organic modifier and the level of silicate dispersion can affect the TOS of the reduced charge clay nanocomposites. Table 3 lists the weight loss data of neat DMBZ-15 and nanocomposites that have been aged for 1000 hours at 288°C.

Table 3

Sample	B12 (% wt loss)	B-18 (% wt loss)	B-DMBZ (% wt loss)
No clay (neat resin)	8.78	8.78	8.78
3% Li-0	9.13	23.55*	10.69
3% Li-130	8.03	11.16	9.41
3% Li-150	7.20	11.13	9.99
3% Li-170	7.86	11.11	9.44

* High weight loss, in this case, may be due to sample processing.

Only the nanocomposites where the clay was exchanged with B12 showed a decrease in weight loss on aging when compared to the neat DMBZ-15 resin. Within this set of data, the nanocomposite containing 3wt% Li-0 had a higher weight loss than the neat resin.

This has been observed in other high temperature polyimide-silicate systems where the silicate modification was an alkyl amine, and the higher weight loss was likely do to degradation of the amine. As the temperature of the heat treated clays increased and thus the amount of organic modifier decreased, the TOS of the nanocomposite improved. This increase in TOS was ~18% for 3% Li-150 ion exchanged with B12.

Nanocomposites prepared from using B18 or B-DMBZ did not show improvement in TOS. In the case of octadecylamine, this may be due to the higher modifier content, by weight, in the octadecylamine clay compared to the dodecylamine clay, as shown in Table 2. It is difficult to determine why the DMBZ clay did not exhibit better TOS, as the modified clay was well dispersed throughout the matrix, and Table 2 reports low modifier content in these clays. An additional concern of the TOS data was the low weight loss for the Li-150 nanocomposite prepared with B12 clay. TGA data for this clay showed an organic content equal to that of Li-0. These issues will be addressed in future work.

Conclusions

Heat treatment of lithium clay was used to prepare clays of decreasing cation exchange capacity. ICP analysis confirmed a lower CEC on increasing temperature of the heated lithium clay. TGA analysis of the ion exchanged clays was mostly in agreement with the ICP data. With the exception of the lithium clay heated at 150°C, the reduced charge clays were exchanged with a decreasing amount of organic modifier. The addition of organically modified reduced charge clays to DMBZ-15 resulted in varying levels of dispersion, where heating at 150°C and 170°C showed the highest levels of

silicate dispersion in the DMBZ-15 matrix. Clays modified with B18 or B-DMBZ also exhibited greater silicate layer dispersion than that of B12. However, the TOS of the B12 based nanocomposites provided the lowest weight loss on aging, when compared to the base resin.

Acknowledgements

The authors would like to thank Linda Inghram for the TOS measurements, Jami Olminsky for ICP analysis, Vic Klans for sample cutting, Ralph Garlick for XRD analysis, and David Hull for TEM analysis. Support for this research was provided by the Highly Loaded Lightweight Compressors and Turbines Project of the Ultraefficient Engine Technologies Project at the NASA Glenn Research Center.

References

1. Alston W, 1995 *High Perform. Polym.* **7** (1) 93
2. Delvigs P, Klopotek DL and Cavano PJ 1994 *High Perform. Polym.* **6** 209
3. Delvigs P, Klopotek DL and Cavano PJ 1997 *High Perform. Polym.* **9** 161
4. Chuang K, Waters J and Hardy-Green D 1997 Proceedings from the 42nd International SAMPE Symposium, May 4-8, 1283
5. Meador MAB, Johnston JC, Frimer A, Gilinsky-Sharon P and Gottlieb H 2001 *Chem. Mater.* ASAP Article
6. Tyan HL, Liu YC and We, KH 1999 *Chem. Mater.* **11** 1942
7. Tyan HL, Liu YC and We, KH 1999 *Polymer*, **40** 4877
8. Lan T and Pinnavaia TJ 1994 *Chem. Mater.* **6** 573

9. Kawasumi M, Hasegawa N, Kato M, Usuki A and Okada A 1997 *Macromolecules* **30** 6333
10. Chen TK, Tien YI and Wei KH 2000 *Polymer* **41** 1345
11. Burnside S and Giannelis EP 1995 *Chem. Mater.* **9** (7) 1597
12. Messersmith P and Giannelis EP 1995 *J. Polym. Sci. A: Polym. Chem.* **33** 1047
13. Delozier DM, Orwoll RA, Cahoon JF, Johnston NJ, Smith Jr. JG and Connell JW 2002 *Polymer* **43** 813
14. Xie W, Gao Z, Liu K, Pan WP, Vaia R, Hunter D and Singh A 2001 *Thermochimica Acta* **367-368** 339
15. Liang ZM, Yin J and Xu HJ 2003 *Polymer* **44** (5) 1391
16. Campbell S and Scheiman D 2002 *High Perfor. Polym.*, **14**, 17
17. Chu LL, Anderson SK, Harris JD, Beach MW and Morgan AB 2004 *Polymer* **45** 4051
18. Hrobarikova J, Madejova J and Komadel P 2001 *J. Mat. Chem.* **11** 1452
19. Chuang K, Papadopoulos D and Ardent C 2002 Proceedings from the 47th International SAMPE Symposium, May 12-16, 1175
20. Delozier DM, Orwoll RA, Cahoon JF, Ladislav JS, Smith Jr. JG and Connell JW 2003 *Polymer* **44** 2231
21. Shi H, Lan T and Pinnavaia TJ 1996 *Chem. Mater.* **8** 1584
22. Meier LP and Nuesch R 1999 *J. Colloid and Interface Sci.* **217** 77

Figures

1. DMBZ-15 synthesis

2. XRD of unheated lithium exchanged clay, lithium exchanged clay heated at 130°C, 150°C, and 170°C.

3. XRD of lithium clay ion exchanged with protonated dodecylamine.

4. XRD of lithium clay ion exchanged with protonated octadecylamine.

5. XRD of lithium clay ion exchanged with protonated DMBZ.

6a-c. XRD of nanocomposites

7a-c TEM of nanocomposites

Tables

1. Cation exchange capacity of reduced charge clays, calculated from ICP data

2. TGA weight loss data of organically modified reduced charge clays

3. TOS data of DMBZ-15 nanocomposites